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Solubility Measurements of Aromatic Hydrocarbons and Carbon Disulfide in Liquid Sulfur by Gas Chromatography

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Sir: The study of liquid solutions of elemental sulfur with various solvents has been undertaken by several investigators during the past 75 years. This research has been collected and interpreted by Scott[2a] in an excellent review. Still, there remains a paucity of thermodynamic studies involving sulfur with nonelectrolyte solutes. Such data are of extreme importance in the devolatilization of hydrocarbons from molten sulfur and the reclamation of sulfur as a commercial by-product from petroleum feedstocks.

Such thermodynamic data may be conveniently determined by using gas chromatography and employing liquid sulfur as the column solvent. Here the mole fraction-based activity coefficient of the solute in the stationary phase is given as

$$\ln \gamma_f^{\infty} = \ln \frac{RT}{Mp_2^{0}V_g^{0}} - \frac{B_{22}p_2^{0}}{RT} \qquad (1)$$

where γ_f^{∞} = fugacity corrected activity coefficient of the solute at infinite dilution in the stationary phase, R = gas constant, T = column temperature in °K, M = molecular weight of the stationary phase, p_2^0 = saturated vapor pressure of the solute, V_g^0 = specific retention volume of the solute in the stationary phase, and B_{22} = second virial coefficient of the pure solute.

Although the use of the mole fraction based γ_f^{∞} may be questioned on the grounds that sulfur in the temperature range of these experiments (between the melting point of sulfur [~118°] and the floor temperature [159°]) consists of several distinct molecular species, conversion to another concentration-activity scale may be readily accomplished.[2b] In this work, we have retained the above convention for theoretical convenience as noted and used by Scott.[3]

A modified Varian Model 1520 gas chromatograph equipped with a flame ionization detector was used to obtain the data in this study. The temperature of the column oven was ascertained by employing an array of copper–constantan thermocouples placed spatially in the volume of the oven occupied by the column. The average short term temperature fluctuation was found to be ±0.1° while the variance from thermocouple to thermocouple was ±0.3°. Helium was used as the carrier gas and its flow rate measured by a soap bubble flow meter. Columns were constructed of 0.25-in. o.d. stainless steel tubing, 4 ft. in length. The stationary phases were supported on 45–60 mesh Chromasorb G.

The sulfur was purified by the method of Bacon and Fanelli[4] and deposited on the support by the method of Urone and Parcher.[5] Tumbling of the coated support material in a stream of dry nitrogen improved the coating uniformity and helped to remove traces of objectable CS_2, H_2S, and SO_2. The coated support was then packed into the stainless steel tubing and purged in the chromatograph for a period of 48 hr with helium. Differential thermal analysis of the sulfur at all stages of the above described operation and on the column support showed identical thermograms.

The degree of stationary phase bleed was checked by measuring the specific retention volume of ethylbenzene at the highest temperature used in this study (153°) and was found not to vary more than 0.5% over a 72-hr period. Reagent grade solutes were employed in all cases and used without further purification. All solutes were injected in

TABLE I: Fugacity Corrected Activity Coefficients at Infinite Dilution and Heats of Solution of Solutes in Molten Sulfur

Solute	γ_f^∞			
Temp, °C	129.5	142.4	152.9	$\Delta H_s{}^a$
Benzene	7.45	7.89	7.14	−7.0
Toluene	9.67	8.62	8.27	−6.2
Ethylbenzene	19.0	16.4	10.6	−8.6
o-Xylene	10.9	9.24	9.28	−7.2
m-Xylene	12.0	10.5	10.3	−8.8
p-Xylene	11.2	10.9	10.8	−8.8
CS_2	1.70	1.64	1.60	−5.6

[a] In kcal/mole.

triplicate, the mean of the retention volumes employed for subsequent calculations. Data were taken at approximately 10° intervals starting at 130°.

The saturated solute vapor pressures were calculated using the Antoine equation employing the regression constants from Dreisbach.[6] Virial coefficients, B_{22}, were computed in the case of the aromatic solutes, from the modified corresponding states equation of McGlashan and Potter[7] using critical constants obtained from the compendia of Dreisbach[6] and Kudchadker, *et al.*[8] The viral coefficient for CS_2 was interpolated from the smoothed data in Dymond and Smith.[9]

Table I lists the activity coefficients for six aromatic solutes and CS_2 in molten sulfur at three different temperatures. In all cases, the activity coefficients are greater than unity, indicating positive deviation from Raoult's law. Of the seven solutes, CS_2 exhibits the most ideal solution with sulfur, a result that is not surprising in view of the high solubility of sulfur in CS_2. For the aromatic solutes, there is an increase in γ_f^∞ with alkylation of the benzene ring, implying that an increase in aliphatic character of the solute will increase its positive deviation from Raoult's law.

The above trends are also verified by the large activity coefficients recorded for the *n*-alkanes (approximately 80 for *n*-decane to 100 for *n*-dodecane at 129.5°) with molten sulfur. These results have not been recorded in Table I since they are probably 20–30% in error due to our failure to correct for solute adsorption at the gas–liquid interface.[10] Still, the γ_f^∞ would be larger for the *n*-alkanes than for the aromatic hydrocarbons on the basis of their respective cohesive energy densities.[11] Research is presently under way to determine γ_f^∞ for the aliphatic hydrocarbons corrected for interfacial adsorption effects.

The temperature dependence of γ_f^∞ is difficult to discern. In most cases γ_f^∞ decreases with temperature, the exception being benzene which shows a high value for γ_f^∞ at 142.4°. This anomolous result may be due to experimental error or more probably due to the strong dependence of the activity coefficient on the second virial coefficient and its temperature derivative.[12,13] The latter statement also probably applies to the slight variation in γ_f^∞ recorded for the xylene isomers as a function of temperature; which compares in magnitude with the results obtained by Newman and Prausnitz[13] for solvent–polymer systems over a similar 20–30° temperature range.

The last column in Table I lists the heats of solution for the various solutes dissolving in molten sulfur. These were calculated from

$$d \ln V_g^0/dT = \Delta H_s'/RT^2 \qquad (2)$$

where $\Delta H_s'$ is equal to the heat of solution of the solute at 0°. To correct $\Delta H_s'$ to the enthalpy of solution at the column temperature, ΔH_s, requires use of

$$\Delta H_s = \Delta H_s' - RT + RT^2\eta \qquad (3)$$

where η is the thermal expansion coefficient of the solvent. Values of η were obtained from the Critical Tables.[14]

The average standard deviation of the enthalpy values in Table I is 11% making comparison on an absolute basis of limited value. However, in all cases ΔH_s for the solute–sulfur interactions is exothermic and less negative than the corresponding heats of vaporization for the respective solutes. As such, the excess heats of solution are all positive, indicating the absence of any strong interaction between the solutes and sulfur. Unfortunately, there are few data with which to compare our results to. Touro and Wiewiorowski[15] have computed a ΔH_s for CS_2 in molten sulfur of −6.42 kcal/mol. This compares favorably with our result of −5.6 kcal/mol.

Presently, we are continuing these studies to include a larger number of solutes which differ in their electron-donating capacity. From this research we hope to obtain evidence to examine the acid–base theory of liquid sulfur proposed by Wiewiorowski and Touro.[16]

References and Notes

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